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(54) **Process for the preparation of esters or salts of aromatic or etheroaromatic acids.**

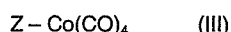
(57) A process for the preparation of esters or salts of aromatic or etheroaromatic acids of formula Y-Ar-CO-OR (I), where:

Ar represents an aromatic group constituted by one or more benzene rings, optionally condensed, or an etheroaromatic nucleus optionally condensed with one or more benzene rings;

Y represents zero, one or more of certain defined substituents (including halogen), which substituents may be the same or different; and

R represents an alkyl group R₁ having up to 5 carbon atoms or an alkali metal or alkaline-earth metal M.

These esters and salts (I) are obtained by reaction of a halide of formula Y-Ar-X (II) where Ar and Y have the defined meanings and where X is Cl, Br or I, with carbon monoxide, in an alcoholic solvent R₁OH at atmospheric pressure and at a temperature from -10° to 60° C in the presence of an acidity-acceptor compound and of a catalyst constituted by a cobalt complex of formula (III):



where Z has certain defined meanings.

The corresponding aromatic or etheroaromatic acids can be obtained by further treatment of the esters and salts thus obtained, by following known procedures.

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"PROCESS FOR THE PREPARATION OF ESTERS OR SALTS OF
AROMATIC OR ETHEROAROMATIC ACIDS"

The present invention relates to a process for the
preparation of esters or salts of aromatic or etheroaromatic
5 acids.

More particularly, the invention relates to a process for
the preparation of esters or salts of aromatic or etheroaromatic
acids of formula (I):



10 where:

Ar represents an aromatic group constituted by one or more
benzene rings, optionally condensed, or by an etheroaromatic
nucleus optionally condensed with one or more benzene rings;

Y represents zero, one or more substituents, which may be
15 the same or different, selected from a halogen; an alkyl group
having up to 6 carbon atoms; an alkoxy group having up to 5
carbon atoms; an ester group $-COOR'$ where R' contains up to
5 carbon atoms; an hydroxyl group; a phenyloxy group optionally
substituted with groups inert under reaction conditions; a
20 trifluoromethyl group; a nitrile group; an amidic group $(-CONH_2)$;
an acetamidic group $(-NH-CO-CH_3)$ or an acyl group $-CO-R''$ where R''
represents a hydrocarbon group having up to 8 carbon atoms; and

R represents an alkyl group R_1 having up to 5 carbon atoms
or an alkali or alkaline-earth metal M.

25 The corresponding aromatic or etheroaromatic acids can be
obtained by further treatment of the esters and salts obtained

by the process of the invention, by following known procedures.

Such esters and their corresponding acids find various applications. They can be used, for example, in the preparation of alkydic resins (benzoic acid), of dyes and pigments (naphthoic acids), of azo-dyes (anthranilic acid) and in the field
5 of plasticizing agents (esters of phthalic acid with higher alcohols).

Processes for the preparation of carboxylic aryllic acids and their esters by carbonylation of aryl halides with carbon
10 monoxide in the presence of a transition metal, for example Ni, Pd or Pt, are known. The reaction generally requires the use of high pressures and temperatures; however, these difficult working conditions adversely affect the economy of such processes, making them unsuitable for industrial application.

15 A variant of the above mentioned processes comprises the use of Ni(CO)_4 catalysts and of special dipolar protonless solvents associated with basic compounds which allow milder working conditions to be utilized. The use of Ni(CO)_4 as catalyst, considering its high volatility and toxicity, is
20 however disadvantageous; another disadvantage of the process lies in the use of expensive solvents.

It has also been proposed to perform carbonylation of aromatic halides in the presence of palladium catalysts with phosphinic ligands, both in homogeneous phase and in phase-
25 transfer conditions. The high cost of the catalyst and the use of phosphinic ligands make this process economically disadvantageous.

Recently, for such carbonylation reaction of aromatic halides, the use of catalytic systems constituted by cobalt salts, alcoholates and sodium hydride has been reported; the use of cobalt carbonyl with simultaneous irradiation with UV light
5 has also been proposed: these are mainly scientific methods for which, at the present time, it is difficult to envisage industrial application.

The present invention aims to provide a simple and economic process for the preparation of esters or salts of aromatic or
10 etheroaromatic acids of formula (I), avoiding the drawbacks of the above mentioned processes. Another aim is to provide a process which may be performed at or near ambient temperature and at atmospheric pressure. It is also desirable that the process may utilize a readily preparable non-toxic catalyst, and that
15 the process may give high selectivity with respect to the desired product.

The present invention provides a process for the preparation of esters or salts of aromatic or etheroaromatic acids of formula $Y-Ar-CO-OR$ (I), where Ar, Y and R are as previously
20 defined, wherein a halide of formula (II):



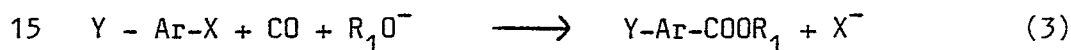
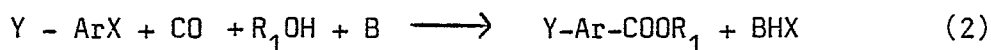
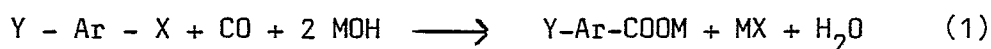
where Ar and Y have the meanings as previously defined and where X is Cl, Br or I, is reacted with carbon monoxide in an alcoholic solvent R_1OH (where R_1 is an alkyl group having up
25 to 5 carbon atoms) at atmospheric pressure and at a temperature from -10° to $60^\circ C$ in the presence of an acidity-acceptor compound and of a catalyst constituted by a cobalt complex of formula (III):



where Z is a group selected from CH_3 ; CH_2F ; CHF_2 ; CF_3 ; CH_2CN ; $\text{CH}_2\text{-COOR}''$ where R'' is an alkyl group having up to 8 carbon atoms or a benzene group, the latter being optionally

5 substituted with groups inert under reaction conditions; and $\text{CH}_2\text{Ar}'$ where Ar' is an aromatic group constituted by from one to three benzene rings optionally condensed and optionally substituted with groups inert under reaction conditions, in particular with electron-attractor groups.

10 The reaction gives rise to the formation of esters or salts, as a function of the nature of the acidity-acceptor compound, according to the reactions hereunder indicated:



In the reaction (1) the acidity-acceptor compound is an alkali or alkaline-earth oxide or hydroxide schematically represented by formula MOH , and a salt is obtained. NaOH , KOH and CaO are among the preferred MOH compounds.

20 In the reaction (2) a weaker

acidity-acceptor compound B is used, preferably Na_2CO_3 or K_2CO_3 , and an ester is obtained. In this case, the solvent R_1OH , where R_1 is an alkyl group having up to 5 carbon atoms, is one of the reagents.

25 In the reaction (3), the acidity-acceptor compound is an alcoholate R_1O^- derived from alcohol R_1OH used as solvent,

and an ester is obtained.

The catalysts $Z-Co(CO)_4$ (III) are mainly known substances in themselves, described in the following publications:

- W Hieber and others, Z. Naturforsch. 13b, 192-4 (1958)
- 5 - W Hieber and others, Z. Naturforsch. 16b, 229-31 (1961)
- E. Lindner and others, Chem. Ber. 107, 1444-1455 (1974)
- V. Galamb and others, Journal of Organometallic Chemistry 209 (1981) 183-195
- V. Galamb and others, J. Chem. Soc., Chem. Commun., 1982,
- 10 487-488.

The process for the preparation of such catalysts is also described in these publications. Usually, they are obtained by reaction, generally in ether solvent, of the alkali metal salts of cobalt hydrocarbonyl with the corresponding organic

15 halides of formula (IV):



where Z and X are as previously defined, or with the anhydrides of formula (V):



20 where Z is as previously defined.

When Z is a CH_2-COOR''' group, R''' is an alkyl group having up to 8 carbon atoms or a benzene group, the latter being optionally substituted with groups inert under reaction conditions; in the latter case, there are preferably from 1 to 3 inert

25 groups, which may be the same or different, chosen in particular from among hydrocarbon groups having up to 8 carbon atoms,

methoxy groups, phenoxy groups and ester groups containing up to 4 carbon atoms.

When Z is a $\text{CH}_2\text{-Ar'}$ group, Ar' is an aromatic group constituted by from one to three benzene rings optionally condensed and optionally substituted with groups inert under reaction conditions, in particular with electron-attractor groups. The inert groups include those already defined hereinabove as well as the electron-attractor groups; the latter are preferred: for example, fluorine, CF_3 , chromotricarbonyl $\text{Cr}(\text{CO})_3$ group and, restricted to the case of benzene nuclei, chlorine are suitable (chlorine, in fact, is not reactive under reaction conditions when it is present on a benzene nucleus). The substituent groups may be the same or different, and preferably there are 1 to 3 of them for each benzene ring. Preferably, there are 1 or 2 benzene rings.

The starting halide Y-Ar-X (II) can contain more than one reactive halogen; in this case more than one -COOR group can replace a halogen. Hence, starting for example from p-dibromobenzene, a salt or an ester or terephthalic acid is obtained.

In the halide (II), Ar represents an aromatic group constituted by one or more benzene rings, optionally condensed, or an etheroaromatic nucleus optionally condensed with one or more benzene rings.

When Ar is an aromatic group with more than one benzene ring, the rings may be linked to each other for example through a direct carbon-carbon link; the rings can be condensed as well. Preferably the Ar group contains from one to three benzene rings.

When Ar is an etheroaromatic nucleus, one or more atoms chosen from N, O and S can be contained in it; for example, pyridine, furane and thiophene nuclei are suitable. The etheroaromatic nucleus can be condensed with one or more benzene nuclei; in this case there are preferably from 1 to 3 benzene nuclei.

In the halide (II), Y represents zero, one or more substituents, preferably from zero to 4 substituents.

When, in the halide (II), Y is a phenyloxy group optionally substituted with groups inert under reaction conditions, these inert groups, which may be the same or different, are chosen in particular from among hydrocarbon groups having up to 8 carbon atoms, methoxy groups, phenoxy groups and ester groups containing up to 4 carbon atoms; preferably there are from 1 to 4 inert groups.

Good results have been obtained for example with the following halides: 2-chloronaphthalene, 2-chlorothiophene, bromobenzene, 1-chloronaphthalene, 4-bromotoluene, 3-bromoanisole, p-dibromobenzene, 4-chlorobromobenzene, 2-chlorobromobenzene, 3-chlorobromobenzene, methyl 2-chlorobenzoate, 2-bromothiophene, 2-bromoacetoanilide, 3-bromopyridine, 3-bromofurane, and 2-hydroxy-6-bromonaphthalene.

The alcoholic solvent R_1OH is an alkyl alcohol containing up to 5 carbon atoms. It is preferably chosen from methyl, ethyl and isopropyl alcohols.

The reaction is carried out at atmospheric pressure and at a temperature ranging from -10° to 60°C , preferably at a temperature ranging from 0° to 40°C . The catalyst, dissolved in a suitable solvent, is preferably added gradually into the
5 reactor containing the other reagents and kept under CO atmosphere; ethers, in particular ethyl ether, hydrocarbons and R_1OH alcohols are for example suitable solvents for the catalyst.

When R_1O^- alcoholate is used, the latter can be prepared
10 separately or produced in situ by reaction of R_1OH alcohol with an alkali metal, in particular sodium.

The molar ratio between halide (II) and catalyst (III) can vary within wide limits, for example 20:1 to 300:1, more preferably from 20: to 200:1.

15 The acidity-acceptor compound is generally introduced according to a substantially stoichiometric ratio with respect to halide (II), according to reaction (I), (2) or (3); however, an excess amount can be used as well, up to approximately 50% with respect to stoichiometry.

20 Complete reaction requires generally from 1 to 12 hours according to the temperature, the concentration of reagents, the nature of the halide (II) and the rate at which the solution containing the catalyst is added.

The process can be effectively performed as follows: the
25 solvent, the acidity-acceptor compound and halide (II) are introduced, in a CO atmosphere into a reactor equipped with a stirrer, a thermometer and a condenser. Once the mixture has

reached the desired temperature, the predetermined amount of catalyst, dissolved in a suitable solvent, is added gradually under stirring. During catalyst addition, the reaction progress is indicated by the absorption of carbon monoxide; 5 the reaction ends when the absorption ceases.

The aromatic or etheroaromatic acid can be obtained from its salt or from its ester by known methods. For example, when the salt is obtained, water is added and the mixture is acidified with a mineral acid, for example HCl. The acid is extracted 10 with a solvent, for example ether. The organic phase thus obtained is in its turn extracted with an aqueous solution of sodium bicarbonate, which is acidified and extracted with ether, which, after evaporation, supplies the acid that can be purified using known methods.

15 When an ester is obtained, it is for example possible to act as follows: the mixture is diluted with water, acidified and then extracted with ether. After ether evaporation, the ester is isolated using known techniques (for example by distillation or crystallization) or can be saponified in acid or basic 20 ambient to give the acid.

The invention will be further described with reference to the following illustrative Examples.

Example 1

30 ml methyl alcohol and 1 g metal sodium were introduced under CO atmosphere into a 100 ml reactor equipped with a magnetic stirrer, a thermometer, a condenser and a dropping
 5 funnel. When all the sodium had reacted, 7.14 g 1-chloro-naphthalene were introduced. The temperature was set at 25°C and a solution of 0.103 g (ethoxy carbonyl)-methyl-cobalt tetracarbonyl $[C_2H_5O-C-\underset{\text{O}}{\underset{||}{CH_2}}Co(CO)_4]$ in 5 ml ethyl ether were

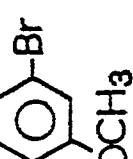
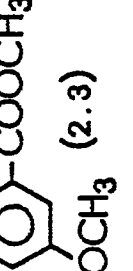
10 introduced through the dropping funnel for one hour.

The solution was left under stirring at 25°C until carbon monoxide absorption ceased (approx. 2 hours), then the reaction mixture was saponified by adding 3 g NaOH and 20 ml water and maintaining boiling for approximately 2 hours. After cooling,
 15 water was added, acidification was carried out with concentrated HCl and extraction was carried out with ether. The organic phase was extracted with bicarbonate-saturated solution and then the aqueous layer was re-acidified and finally extracted with ether. By evaporation of the solvent under vacuum, 3.75 g
 20 1-naphthoic acid were obtained. The remainder was non-reacted product.

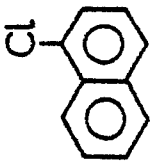
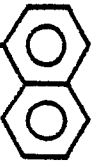
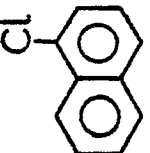
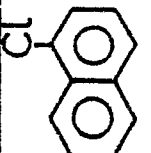
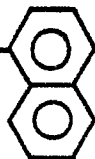
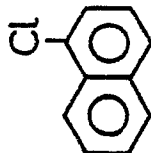
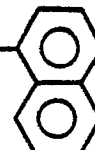
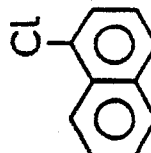
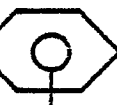
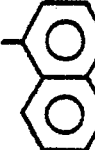
The number of CO moles introduced into the product per Co mole was 54.7.

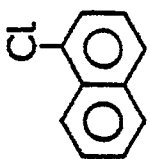
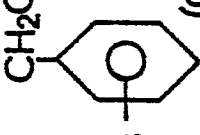
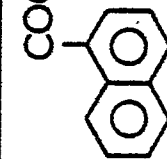
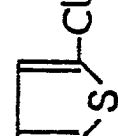
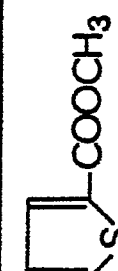
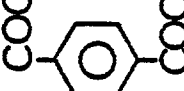
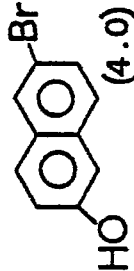
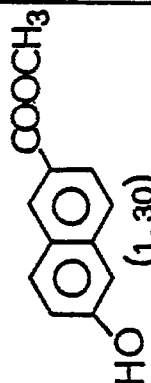
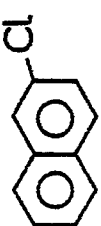
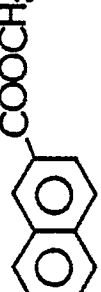
Examples 2-25

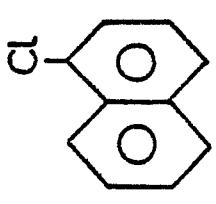
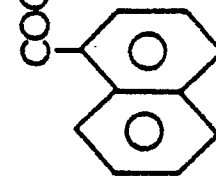
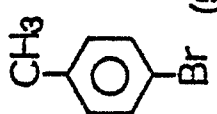
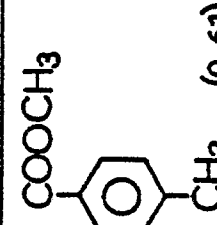
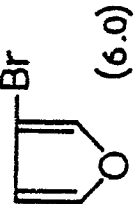
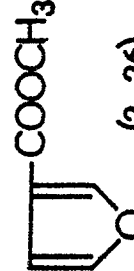
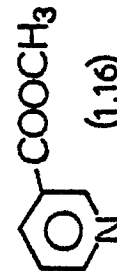
Using the same equipment as described in Example 1, Examples 2-25 were carried out wherein the relevant reactants and reaction conditions are given in the following Table.

Example	Halide (g)	Catalyst (g)	Solvent	Acidity- acceptor compound	Temperature (°C)	Product (g)	Number of CO moles introduced into the product per Co mole.
2	 (3.4)	$C_2H_5OCOCH_2Co(CO)_4$ (0.08)	CH_3OH	$NaOCH_3$ (2.3)	17	 (2.53)	26
3	 (1.6)	$FCH_2Co(CO)_4$; (0.057)	CH_3OH	$NaOCH_3$ (0.82)	22	 (0.91)	24
4	 (3.75)	$C_2H_5OCOCH_2Co(CO)_4$ (0.119)	CH_3OH	$NaOCH_3$ (2.5)	25	 (2.00)	32
5	 (3.75)	$C_2H_5OCOCH_2Co(CO)_4$ (0.095)	CH_3OH	$NaOH$ (2.5)	25	 (1.2)	27
6	 (4)	$C_2H_5OCOCH_2Co(CO)_4$ (0.072)	CH_3OH	$NaOCH_3$ (2.0)	25	 (2.3)	49

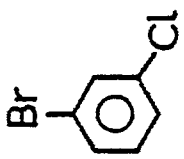
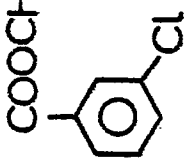
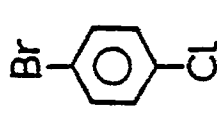
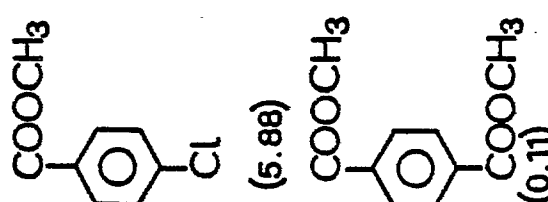
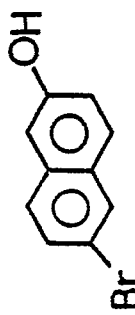
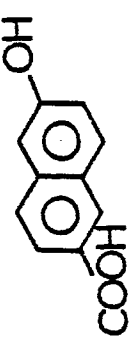
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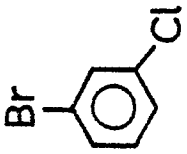
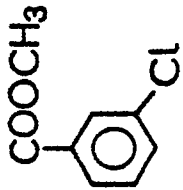
7	 (7.14)	$\text{FCH}_2 \text{ Co(CO)}_4$ (0.098)	CH_3OH	NaOCH_3 (2.3)	25	 COOCH_3 (4.2)	47
8	 (7.14)	$\text{FCH}_2 \text{ Co(CO)}_4$ (0.112)	$\text{C}_2\text{H}_5\text{OH}$	NaOC_2H_5 (3.0)	25	 COOC_2H_5 (3.7)	34
9	 (7.14)	$\text{C}_2\text{H}_5\text{OCOCH}_2\text{Co(CO)}_4$ (0.119)	$\text{C}_2\text{H}_5\text{OH}$	NaOC_2H_5 (3.0)	25	 COOC_2H_5 (4.65)	50.4
10	 (7.14)	$\text{C}_2\text{H}_5\text{OCOCH}_2\text{Co(CO)}_4$ (0.115)	i. $\text{C}_3\text{H}_7\text{OH}$	NaOC_3H_7 (3.6)	35	 COOC_3H_7 (1.74)	18.5
11	 (7.14)	Cr(CO)_3 —  $\text{CH}_2\text{Co(CO)}_4$ (0.066)	CH_3OH	NaOCH_3 (2.3)	25	 COOCH_3 (1.5)	49

12	 (7.14)	$\text{Cr}(\text{CO})_3$	 $\text{CH}_2\text{Co}(\text{CO})_4$ (0.079)	CH_3OH	NaOCH_3 (2.3)	10	 COOCH_3 (2.05)	56
13	 (3.2)	$\text{C}_2\text{H}_5\text{OCOCH}_2\text{Co}(\text{CO})_4$ (0.083)	CH_3OH	CH_3OH	NaOCH_3 (2.3)	25	 COOCH_3 (3.0)	65
14	 $\text{Br}-\text{Br}$ (5.2)	$\text{C}_2\text{H}_5\text{OCOCH}_2\text{Co}(\text{CO})_4$ (0.114)	CH_3OH	CH_3OH	NaOCH_3 (2.6)	25	*  COOH (2.8)	60
15	 Br (4.0)	$\text{C}_2\text{H}_5\text{OCOCH}_2\text{Co}(\text{CO})_4$ (0.055)	CH_3OH	CH_3OH	NaOCH_3 (2.3)	45	 COOCH_3 (1.30)	30
16	 Cl (7.14)	$\text{C}_2\text{H}_5\text{OCOCH}_2\text{Co}(\text{CO})_4$ (0.178)	CH_3OH	CH_3OH	K_2CO_3 (7.5)	25	 COOCH_3 (2.7)	21

17	 (7.14)	$C_2H_5OCOCH_2Co(CO)_4$ (0.060)	CH ₃ OH	NaOCH ₃ (2.3)	0	 (1.3)	30
18	 (5.95)	$C_2H_5OCOCH_2Co(CO)_4$ (0.094)	CH ₃ OH	NaOCH ₃ (2.1)	25	 (0.61)	11.1
19	 (6.0)	$C_2H_5OCOCH_2Co(CO)_4$ (0.073)	CH ₃ OH	NaOCH ₃ (2.3)	25	 (2.26)	56.4
20	 (6.6)	$C_2H_5OCOCH_2Co(CO)_4$ (0.087)	CH ₃ OH	NaOCH ₃ (2.3)	25	 (1.16)	24.8
21	 (8.6)	$C_2H_5OCOCH_2Co(CO)_4$ (0.083)	CH ₃ OH	NaOCH ₃ (2.3)	25	 (3.4)  (0.570)	80

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22	 (8.6)	$C_2H_5OCOCH_2Co(CO)_4$ (0.042)	CH_3OH	$NaOCH_3$ (3.05)	25	 (6.0)	216
23	 (8.6)	$C_2H_5OCOCH_2Co(CO)_4$ (0.074)	CH_3OH	$NaOCH_3$ (3.05)	25	 (5.88) (0.11)	125
24	 (3.0)	$C_2H_5OCOCH_2Co(CO)_4$ (0.115)	CH_3OH	$NaOH$ (2.0)	25	 (1.2)	14

25	 (8.6)	$\text{CNCH}_2\text{Co(CO)}_4$ (0.049)	CH_3OH	NaOCH_3 (3.05)	25	 (3.26)	82
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* after saponification (see Example 14)

CLAIMS

1. A process for the preparation of esters or salts of aromatic or etheroaromatic acids of formula (I):



5 where:

Ar represents an aromatic group constituted by one or more benzene rings, optionally condensed, or by an etheroaromatic nucleus optionally condensed with one or more benzene rings;

Y represents zero, one or more substituents, which may be
 10 the same or different, selected from a halogen; an alkyl group having up to 6 carbon atoms; an alkoxy group having up to 5 carbon atoms; an ester group $-COOR'$ where R' contains up to 5 carbon atoms; a hydroxyl group; a phenyloxy group optionally substituted with groups inert under reaction conditions; a
 15 trifluoromethyl group; a nitrile group; an amidic group $(-CONH_2)$; an acetamidic group $(-NH-CO-CH_3)$ or an acyl group $-CO-R''$ where R'' represents a hydrocarbon group having up to 8 carbon atoms; and

R represents an alkyl group R_1 having up to 5 carbon atoms
 20 or an alkali or alkaline-earth metal M; characterized in that a halide of formula (II)



where Ar and Y have the hereinabove defined meaning and where X is Cl, Br or I, is reacted with carbon monoxide in an
 25 alcoholic solvent R_1OH (where R_1 is an alkyl group having up to 5 carbon atoms) at atmospheric pressure and at a temperature

from -10°C to 60°C in the presence of an acidity-acceptor compound and of a catalyst constituted by a cobalt complex of formula (III):



5 where Z is a group selected from CH_3 ; CH_2F ; CHF_2 ; CF_3 ; $\text{CH}_2\text{-CN}$; $\text{CH}_2\text{-COOR}''$ where R'' is an alkyl group having up to 8 carbon atoms or a benzene group, the latter being optionally substituted with groups inert under reaction conditions; and $\text{CH}_2\text{-Ar}'$ where Ar' is an aromatic group constituted by from one
10 to three benzene rings optionally condensed and optionally substituted with groups inert under reaction conditions, in particular with electron-attractor groups.

2. A process as claimed in claim 1, characterised in that the acidity-acceptor compound is an alkali or alkaline-
15 earth metal oxide or hydroxide and in that a salt is obtained.

3. A process as claimed in claim 1, characterised in that the acidity-acceptor compound is Na_2CO_3 or K_2CO_3 and in that an ester is obtained.

4. A process as claimed in claim 1, characterised in
20 that the acidity-acceptor compound is an alcoholate R_1O^- derived from alcohol R_1OH used as solvent and in that an ester is obtained.

5. A process as claimed in any of claims 1 to 4, characterised in that the alcohol R_1OH is selected from methyl,
25 ethyl and isopropyl alcohol.

6. A process as claimed in any of claims 1 to 5, characterised in that the reaction is performed at a temperature from 0° to 40°C.

7. A process as claimed in any of claims 1 to 6, characterised in that the catalyst, dissolved in a solvent, is added gradually into the reactor containing the other reagents and kept under CO atmosphere.

5 8. A process as claimed in claim 7, characterised in that the catalyst solvent is an ether, a hydrocarbon or an alcohol R_1OH .

9. A process as claimed in claim 8, characterised in that the ether is ethyl ether.

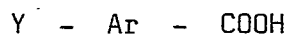
10 10. A process as claimed in any of claims 1 to 9, characterised in that the molar ratio between halide (II) and catalyst (III) is from 20:1 to 300:1.

11. A process as claimed in claim 10, characterised in that the molar ratio between halide (II) and catalyst (III)
15 is from 20:1 to 200:1.

12. A process as claimed in any of claims 1 to 11, characterised in that the molar ratio between the acidity-acceptor compound and halide (II) is from the stoichiometric value to 50% excess with respect to the stoichiometric value.

20 13. Esters or salts of aromatic or etheroaromatic acids of formula $Y - Ar - CO - OR$ (I), wherein Ar, Y and R are as defined in claim 1, characterised by being prepared by a process as claimed in any of claims 1 to 12.

14. A process for the preparation of aromatic or
25 etheroaromatic acids of formula



where Ar and Y are as defined in claim 1, characterised in

that an ester or salt of an aromatic or etheroaromatic acid prepared by the process as claimed in any of claims 1 to 12 is further treated to obtain the corresponding acid.



European Patent
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EUROPEAN SEARCH REPORT

0112679
Application number

EP 83 30 7557

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
A	FR-A-2 286 126 (DYNAMIT NOBEL) * Page 2, line 35 - page 3, line 8; pages 10-11, claims 1,4,6 *	1	C 07 C 69/76 C 07 C 67/36 C 07 C 69/78 C 07 C 69/92 C 07 C 65/11 C 07 C 69/94
A	US-A-2 565 462 (W.W. PRICHARD) * Column 2, lines 42-48; column 3-4, example 1; column 6, claim 1 *	1	C 07 C 63/06 C 07 D 333/40 C 07 C 63/36 C 07 D 333/38 C 07 C 63/26 C 07 D 213/55 C 07 C 51/10 C 07 C 69/80
			TECHNICAL FIELDS SEARCHED (Int. Cl. ³)
			C 07 C 69/00 C 07 C 67/00 C 07 C 51/00 C 07 C 63/00 C 07 C 65/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19-03-1984	Examiner KINZINGER J.M.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	